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Characterization of Ornamental Rock Residue and Potassium Liberation Via Organic Acid Application

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ABSTRACT: Organic acids present in organic matter and, or, exudates by microorganisms and plants can increase the liberation of potassium present in minerals. The objective of this study was to characterize the residue from ornamental rocks and evaluate the release of K from these residues after the application of organic acids. The experiment was conducted under laboratory conditions and followed a 2 × 3 × 5 factorial design with three replicates. The studied factors were: two organic acids (citric acid and malic acid), three ornamental rock residues (R1, R2 and R3) and five organic acid rates (0, 5, 10, 20 and 40 mmol L^{-1}). After agitation, K concentrations were determined in the equilibrium solution. Successive extractions were performed (1, 5, 10, 15, 30 and 60 days after the start of the experiment). The organic acids used (citric and malic) promoted the release of up to 4.86 and 4.34 % of the total K contained in the residue, respectively, reinforcing the role of organic acids in the weathering of minerals and in providing K to the soil. The K quantities were, on average, 6.1 % higher when extracted with citric acid compared to malic acid.

Keywords: stonemeal, fertilization, citric acid, silicate rocks.

INTRODUCTION

Brazilian business transactions in the ornamental rock production chain are estimated by Abirochas (Brazilian Association for Dimension Stones) at $5.5 billion, creating about 130,000 direct jobs in about 10,000 companies (DNPM, 2014). The state of Espírito Santo stands out in the domestic market with over 90 % of Brazilian industry investments in the ornamental rock sector, being the largest producer, processor and exporter in the country, and extracting more than 800,000 m^3 of rock in the state a year. This accounts for about 8 % of the gross domestic product (GDP) of the state (Vitória Stone Fair, 2013).

Due to the large volume of extracted and processed rocks, large amounts of residue are generated. These residues generate an environmental problem of major proportions, occupying increasingly large areas, and fueling concerns about their storage, management and destination. In this context, the use of rock residue in agriculture has been studied for recycling possibilities, since it does not present soil, water and plant contamination potential (Fyfe et al., 2006; van Straaten, 2006; Guarçoni and Fanton, 2011).

The use of rock residue in agriculture is a modern technique used in many countries as a restorer of soil characteristics and supplier of nutrients for plants (Theodoro and Leonardos, 2006; van Straaten, 2006), such as P, K, Ca, Mg and micronutrients. The agronomic use of these residues, as a source of nutrients for soil and plants, is an alternative for their use. Rock residue can be used as a source of gradual nutrient release (Cola and Simon, 2012), which is a desirable feature when considering the most lasting fertilizer effects and the lowest loss risk compared to soluble fertilizers, which are easily lost by leaching and adsorption by soil particles (Nunes et al., 2014). Although they provide fewer nutrients in the short term when compared to highly soluble fertilizers, alternative sources have high residual power in the soil (Resende et al., 2006) and are able to provide nutrients for a period of up to five years after incorporation, as noted by Theodoro and Leonardos (2006).

Rocks with high levels of nutrients may be used for the production of salts or direct application to the soil as slow-release fertilizers. These materials can also be subjected to biological, chemical and, or, physical treatments, which would increase the nutrient availability. The rate and nature of the nutrient liberation from the rocks are governed by many variables, such as source material type, particle size, leaching conditions, pH of the medium and biological activity, among others (Martins et al., 2004). Knowledge of the rates and transformation mechanisms (weathering) of these rocks contributes to better use of the nutrients released in agro-ecosystems. The relative liberation rates of K-bearing minerals vary with the liberation mechanisms. The role organic acids in affecting the soil K supply deserve special attention (Song and Huang, 1988).

Evaluating the role of organic acids on mineral and rock weathering is fundamental for a better understanding of biochemical cycles (Song and Huang, 1988). Furthermore, silicate rocks are considered to have high agricultural potential, such as for alternative slow release fertilizers (Theodoro et al., 2006). Research has evaluated granite mining residue (Guarçoni and Fanton, 2011), volcanic tuff (Theodoro, 2000) and basalts (Almeida et al., 2006). The results show improvements in soil properties and nutrient availability to plants, especially in longer cycle crops.

Knowledge of the effect of organic acids on rock dissolution kinetics and mineral and nutrient availability is a prerequisite for assessing their potential benefit (Harley and Gilkes, 2000). Organic acids present in soil organic matter and, or, exuded by microorganisms and plants, as well as the completion of the composting process including the residue, can facilitate the release of nutrients by the formation of organic-metallic complexes (Tam, 1986), or by releasing H^+ (Harley and Gilkes, 2000). Assuming that the addition of organic acids, depending on their type and quantity, increases the release rate of K present in minerals and rocks, the objective of this study was to evaluate the liberation (quantity and time) of K within ornamental rock residue after the application of citric and malic acid.

MATERIALS AND METHODS

Three samples of ornamental rock residue were collected. The rock came from granite cutting facilities at three different companies in the municipality of Cachoeiro de Itapemirim, ES, and was identified as ornamental rock residue (R1, R2 and R3). Each sample was randomly collected from piles of residue located below the filter presses that had formed after two days of rock sawing; 20 single samples of approximately 1 kg were collected to form a composite sample. The collected residue was dried in an oven (70 °C), passed through a sieve of 48 mesh (0.297 mm), and quartered to obtain a 2 kg sample. The samples were chemically (Table 1) and mineralogically (Figure 1) characterized at the Mineral Technology Centre (CETEM) in Rio de Janeiro, RJ. The opening of the samples for total digestion was performed via wet digestion using HCl, HNO_3 and HF in a microwave oven.

The X ray diffractograms (XRD) of the rock residue samples were obtained by the powder method, analyzed in a Bruker-D4 Endeavor equipment, under the following operating conditions: Co Ka (35 kV/40 mA) radiation; goniometer speed of 0.02° 2Ө per step with time of 1 s per step and collected from 4 to 50° 2Ө. The qualitative interpretations of the spectrum were made by comparison with standards contained in the PDF02 database in the Bruker DiffracPlus software.

The experiment was conducted in the chemical analysis laboratory at the Agricultural Sciences Center of the Federal University of Espírito Santo in the city of Alegre – ES, and followed a randomized block design, conducted in a 2 × 3 × 5 factorial with three replications. The factors under study consisted of two organic acids (citric acid and malic acid, both P.A. reagents), three ornamental rock residues (R1, R2 and R3) and five organic acid rates (0, 5, 10, 20 and 40 mmol L^{-1}), established in accordance with the values found in the literature (Jones, 1998; Andrade et al., 2003; Pires and Mattiazzo, 2007; Corrêa et al., 2008). Samples containing 25 g of each rock residue were stored in plastic 500 mL bottles, and placed in contact with 250 mL of the organic acid solution at different concentrations and shaken on an orbital shaker for a period of 10 min at 175 rpm, and were then allowed to rest for the appropriate time interval for each extraction.

Table 1. Chemical composition of the ornamental rock residue

Composition	Residue 1	Residue 2	Residue 3
	dag kg^{-1}		
SiO_2[1]	68.7	55.0	60.8
Al_2O_3[2]	10.8	14.3	12.6
Fe_2O_3[3]	5.2	6.9	7.9
P_2O_5[4]	0.15	0.36	0.33
TiO_2[4]	0.18	1.00	0.76
Na_2O[3]	2.3	3.9	3.2
K_2O[3]	3.4	3.0	2.6
CaO[2]	1.8	3.8	3.7
MgO[3]	0.29	1.4	1.2
	mg kg^{-1}		
Cd[2]	<10.0	<10.0	<10.0
Pb[2]	<250.0	<250.0	<250.0
Cr[2]	22.4	28.3	15.9
Hg[2]	<0.94	<0.94	<0.94
Cu[3]	<50.0	<50.0	<50.0
Zn[3]	<50.0	92.2	69.8

[1] Gravimetry; [2] Flame atomic absorption spectrophotometry with $C_2H_2/N_2O/ar$; [3] Flame atomic absorption with C_2H_2/air; [4] UV-visible molecular absorption spectrometry.
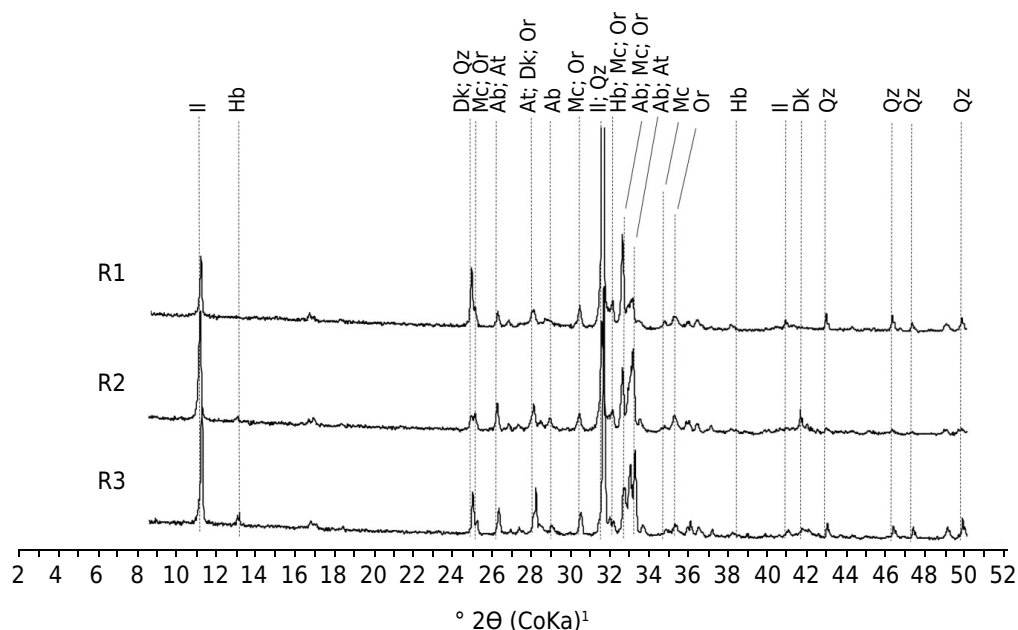
Figure 1. X ray diffraction, chemical composition, interplanar distance and minerals composing the rock residues (R1, R2 and R3). Quartz (Qz), Illite (II), Hornblende (Hb), Dickite (Dk), Anorthite (At), Microcline (Mc), Orthoclase (Or), Albite (Ab).

Successive extractions were carried out 1, 5, 10, 15, 30 and 60 days after the start of the experiment. After centrifugation, the supernatant was collected for analysis of the potassium content in solution. After each extraction period, the organic acid solutions were again prepared and 250 mL was added to the bottles and agitated as described above. The K concentrations in the supernatant (equilibrium solution) were determined by emission spectrometry, according to Claessen (1997).

Data were subjected to analysis of variance since the effects within the qualitative factors (residue, organic acids and interactions among residues within each organic acid) were deployed in orthogonal contrasts. For the quantitative factor (organic acid rates), regression models were adjusted using SAEG statistical software.

RESULTS AND DISCUSSION

The ornamental rock residues presented differences in the concentrations of oxides in their composition, mainly in terms of Si, Al, Fe, K and Ca (Table 1). The physical, physicochemical, chemical and mineralogical characteristics of basalt residue derived from mining activities were studied by Nunes et al. (2014), and showed that oxides of rock residues can release nutrients, acting as a fertilizer.

In the X ray diffraction analysis of the residue samples (Figure 1), the different peaks corresponding to crystalline phases of the minerals present in the samples are shown. The residues exhibited characteristic peaks of quartz and feldspar, which corroborates with the high SiO_2 and Al_2O_3 content in their chemical composition (Table 1), characterizing them as silicate rocks, since it this was a mostly granite residue. The mineral compositions of the studied residues were similar, but we noted that the half widths of the peaks of the minerals, indicating their intensity, were different (Figure 1).

Residue 1 (R1), according to the X ray analysis, contained the minerals quartz (SiO_2); the micas dickite [$Al_2Si_2O_5(OH)_4(HCONH_2)$] and illite [$(KH_3O)Al_2Si_3AlO_{10}(OH)_2$], the plagioclase feldspars albite [$(Na,Ca)Al(Si,Al)_3O_8$] and anorthite [$(Ca,Na)(Si,Al)_4O_8$]; and the alkali feldspars orthoclase ($KAlSi_3O_8$) and microcline ($KAlSi_3O_8$). When comparing R1 to R2 and R3, the quartz, orthoclase and microcline minerals presented peaks of

greater intensity in R1 (Figure 1). Microcline and orthoclase are chemically identical feldspars, but with different crystalline structures (polymorphisms). Both have K in their crystalline structure, intensifying the K_2O content present in the chemical composition of R1 (Table 1).

The mineral hornblende $[K_3Na_5Ca_{1,7}Mg_{3,6}Fe_{1,1}Fe_5Ti_2Al_{1,9}Si_{5,4}O_{22}(OH)]$ of the amphibole group was identified by X ray diffraction only in R2 and R3. This mineral has magnesium in its crystalline structure, which corroborates the higher levels of this element in these residues (Table 1). Hornblende has structural K and can be an important source of this element when present in rocks (Melo et al., 2009).

A higher amount of liberated K was observed for Residue 1 compared to Residues 2 and 3, regardless of the organic acid and the rate used (Table 2). This result was confirmed by significant, positive values in the contrasts tested (C1 and C2, Table 3).

The degree of resistance of the minerals enables different K solubilization mechanisms and the K liberation from more weathered minerals could be attributed to H^+ of the organic acid that attacked the minerals, solubilizing K^+. The rate of K release from biotite indicates that the high ionization of oxalic acid H^+ resulted in high K liberation (Tu et al., 2007). In addition, at a low pH, the release of K from biotite, muscovite and phlogopite was promoted, while the liberation from microcline decreased (Tu et al., 2007).

The contrast C1 (R1 + R2 *vs.* R3) presents positive and significant values, demonstrating that the concentration of K extracted was higher for (R1 + R2) in all samples (Table 3). This is due to the lower amount of K_2O in R3 and a silica content very similar to the other residues, which hindered the chemical modification of the mineral and K liberation.

In contrast C2 (R1 *vs.* R2, Table 3), R1 was, in general, statistically higher in the concentration of K extracted than R2. These results can be explained by the K_2O concentration (R1 = 3.4 dag kg^{-1} and R2 = 3.0 dag kg^{-1}) present in the ornamental rock residue (Table 1), and the mineral type present in these residues, influencing the K liberation rates (Figure 1). The liberation potential of the K contained in rock, residue and soil, depends on the amount of primary and secondary mineral K sources, as well as their weathering potential (Alves et al., 2013). The main minerals related to K availability in Brazilian soils are potassium feldspars, micas, vermiculites and smectites (Curi et al., 2005); the first two are the main constituents of the residues studied here.

The dynamics of K liberation into different fractions in Canadian soils, over a period of 3,200 h, was studied by Simard et al. (1992), via 15 sequential extractions with 0.5 mmol L^{-1} citric acid. These authors observed that the K quantities and liberation rates were obtained in the silt fraction containing various K source minerals, such as feldspar and mica. According to the authors, the mica concentration decreases with decreasing size of the particle size fraction, and the trioctahedral micas (biotite and phlogopite) usually weather faster than the dioctahedral micas (muscovite).

With the X ray diffraction analysis of R1, we observed the crystalline phases of the minerals which are K sources, such as mica, and K-feldspar (microcline and orthoclase) (Figure 1). In tropical conditions, soils present traces of K-feldspar, due to its easy weathering (Martins et al., 2004), causing the rock residue to be a potential source of such minerals and, consequently, of K, from either its direct application or chemical (Carpenter et al., 2007) and physical treatment (Suzuki et al., 2003). Most dissolution reactions of silicate minerals depend on the interactions between the ions on the surface of the mineral. These interactions involve surface oxy-hydroxide groups such as H^+ and OH^- (surface protonation) and ligands, like anions of weak acids, which dominate the dissolution reactions (Martins et al., 2004).

Table 2. Average concentrations of potassium extracted from the rock residues (R) according to the application of organic acids (CA – citric acid and MA – malic acid), extracted with different sampling times

Acid	Rate	Collection							K extracted from the rock
		1ª	2ª	3ª	4ª	5ª	6ª	Total	
	mmol L^{-1}				mg kg^{-1}				%
					Residue 1				
	0	129.0	258.0	136.0	76.3	54.0	39.3	692.7	2.46
	5	281.0	322.0	174.0	111.0	70.3	58.0	1016.3	3.60
CA	10	295.0	364.0	188.0	108.0	61.0	41.7	1057.3	3.75
	20	270.0	397.0	198.0	106.0	69.3	48.3	1088.7	3.86
	40	340.0	478.0	239.0	133.0	76.0	103.0	1369.3	4.86
	Average	263.0	364.0	187.0	107.0	66.1	58.1	1044.9	3.71
	0	148.0	256.0	117.0	78.3	58.0	39.7	697.0	2.47
	5	250.0	332.0	153.0	93.3	78.3	72.3	978.3	3.47
MA	10	261.0	366.0	188.0	106.0	74.7	46.3	1042.7	3.70
	20	286.0	399.0	199.0	88.7	61.7	38.7	1073.0	3.80
	40	344.0	452.0	221.0	93.0	63.7	50.7	1223.7	4.34
	Average	258.0	361.0	176.0	91.9	67.3	49.5	1002.9	3.56
	Average of R1	260.0	362.0	181.0	99.4	66.7	53.8	1023.9	3.63
					Residue 2				
	0	81.0	214.0	110.0	51.0	39.0	28.0	523.0	2.10
	5	184.0	257.0	140.0	82.0	71.0	63.3	797.0	3.20
CA	10	193.0	298.0	165.0	93.7	69.7	59.3	878.0	3.53
	20	211.0	327.0	160.0	93.7	78.0	76.7	946.0	3.80
	40	267.0	343.0	161.0	99.7	100.0	138.0	1108.3	4.45
	Average	187.0	288.0	147.0	84.0	71.6	73.1	850.5	3.42
	0	86.7	207.0	104.0	51.3	36.0	27.7	513.0	2.06
	5	135.0	251.0	145.0	73.3	64.7	80.7	750.0	3.01
MA	10	143.0	273.0	142.0	84.3	69.3	67.7	780.3	3.13
	20	209.0	295.0	151.0	84.3	68.3	63.0	871.0	3.50
	40	248.0	324.0	144.0	81.3	82.3	93.3	972.7	3.91
	Average	164.0	270.0	137.0	74.9	64.1	66.5	777.4	3.12
	Average of R2	176.0	279.0	142.0	79.5	67.9	69.8	813.9	3.27
					Residue 3				
	0	71.7	178.0	94.3	44.0	30.3	21.0	439.3	2.04
	5	173.0	215.0	107.0	64.7	45.3	34.3	638.3	2.97
CA	10	166.0	233.0	109.0	64.7	41.7	34.3	648.7	3.02
	20	172.0	245.0	108.0	63.3	49.3	39.7	677.7	3.15
	40	196.0	267.0	129.0	73.3	63.3	76.7	805.0	3.74
	Average	156.0	228.0	109.0	62.0	46.0	41.2	641.8	2.99
	0	91.7	182.0	90.7	44.7	28.3	21.0	458.7	2.13
	5	173.0	210.0	92.0	53.7	40.0	39.0	607.7	2.83
MA	10	156.0	230.0	108.0	55.0	40.0	35.7	625.0	2.91
	20	135.0	241.0	121.0	58.0	37.7	35.0	627.3	2.92
	40	197.0	264.0	121.0	59.3	44.7	47.0	732.7	3.41
	Average	151.0	225.0	107.0	54.1	38.1	35.5	610.3	2.84
	Average of R3	153.0	227.0	108.0	58.1	42.1	38.4	626.0	2.91

Table 3. Orthogonal contrasts (C) of the amount of potassium extracted considering the residue (R) and organic acids, for each collection time

Residue	Organic Acid	C1	C2	C3	C4	C5
R1	Citric acid	1	1	1	0	0
	Malic acid	1	1	-1	0	0
R2	Citric acid	1	-1	0	1	0
	Malic acid	1	-1	0	-1	0
R3	Citric acid	-2	0	0	0	1
	Malic acid	-2	0	0	0	-1
		Contrast analyzed				
		mg kg^{-1}				
	Collection 1	259.7**	169.5**	5.1^{ns}	22.7**	5.0^{ns}
	Collection 2	376.9**	166.8**	3.1^{ns}	17.5**	2.4^{ns}
	Collection 3	214.8**	78.0**	11.3**	9.7**	2.7^{ns}
	Collection 4	125.5**	39.9**	15.1**	9.1**	7.9**
	Collection 5	100.9**	-2.3^{ns}	-1.1^{ns}	7.5**	7.9**
	Collection 6	93.8**	-31.9**	8.6**	6.7**	5.7**
	Total	1,171.5**	419.9**	41.9**	73.1**	31.5**

C1 = R1+R2 *vs.* R3; C2 = R1 *vs.* R2; C3 = CA *vs.* MA; C4 = CA *vs.* MA; C5 = CA *vs.* MA; CA: citric acid; MA: mMalic acid; ^{ns}: not significant; ** and *: significant at 1 and 5 %, respectively.

The release of K from the ornamental rock residues studied, regardless of the acid and the rate used, was in the following order: R1> R2> R3. The solubilization order of the main cations from silicate minerals weathered by organic acids suggests that the position of cations in the crystal is a dominant factor, and the complexation ability of acids by different cations also determines, to some extent, the cation liberation order (Barman et al., 1992).

By analyzing the released K concentrations, in the third collection the ornamental rock residue R1, R2 and R3 released 77.2; 69.6; 73.5 % of the total K extracted by the end of the experiment, respectively, when citric acid is used at a rate of 40 mmol L^{-1}. For malic acid, these values were 83.2; 73.6; 79.4 %, respectively. The speed at which K is released depends on the mineral type, particle size and its weathering degree, as well as the presence of these organic acids that act on the residue during the mineral decomposition process.

The highest amount of K relative to the total content of the ornamental rock residues R1, R2 and R3 at the end of the experiment was achieved with a rate of 40 mmol L^{-1}, respectively liberating 4.86, 4.45 and 3.74 % K when using citric acid and 4.34, 3.91 and 3.41 % K when malic acid was used (Table 2).

Potassium liberation was most effective in the first three samples (10 days), suggesting that the extractors (organic acids) released K from sites closer to the surface of the mineral (less specific adsorption sites) situated on edges or in the interlayers, close to the edges of the particles. These results corroborate those found by Song and Huang (1988), who studied the K liberation kinetics of pure minerals (biotite, muscovite, microcline and orthoclase) by oxalic acid and found a quick release in a short period. According to the authors, the exposure of K^{+} ions on the surface of the mineral particles, as well as the possibility that during the sample preparation process there was some kind of damage to the mineral structure close to the particle surface, facilitates the access of the extractor to K situated in the mica interlayers or in the feldspar interstices, increasing the liberation of K into the solution.

As the extraction time increases, the solubility caused by the action of organic acids moves toward the center of the particles, where K is more strongly retained, which leads to a marked decrease in the release rate of the nutrient (Castilhos and Meurer, 2001). At that time, the release of K becomes controlled by the K diffusion rate, in the interlayers of the particle center toward the outer edges of the partially weathered minerals.

The average amount of K extracted from residues R1, R2 and R3, adding all collection phases, was considered low, with values of 3.63, 3.27 and 2.91 %, respectively, independent of the organic acid and the rate used (Table 2). However, environmental factors such as temperature, biological action, soil characteristics, incubation time and plant type can increase the amount of nutrients released from rock residue (Harley and Gilkes, 2000; Wang et al., 2000; Stanford et al., 2008).

Most minerals that have K in their structure, present it in insoluble form, so there is difficulty in obtaining this element, as in the case of silicates (Nascimento and Loureiro, 2004). Despite its slow dissolution, ornamental rock residue may also contribute as a source of nutrients to plants (Silva et al., 2012). This slow, gradual release may be in tune with crop demand, particularly long-cycle crops, thereby reducing K losses via leaching in the soil, as occurs when the element is provided through readily soluble fertilizers. This timing is very important, especially in the tropics, where K leaching is intense (Werle et al., 2008).

While evaluating an agroforestry system, Theodoro et al. (2013) used sediments that accumulated in the Tucuruí water reservoir (Pará, Brazil) to remineralize degraded soils of its surroundings together with crushed rock with or without the addition of NPK and organic compost. Their studies showed that greater plant growth and productivity were obtained in the portions where a mixture of sludge, ground rock and organic compost was added. Many plants exude low molecular weight organic acids, such as citric acid, in their rhizosphere, and may accelerate the solubilization of rock dust and thereby increase the nutrient availability for absorption by the roots (Harley and Gilkes, 2000). The concentration of organic acids of the soil rhizosphere is high in relation to other components of root exudates, with concentrations up to 50 mmol L^{-1} at a distance of 1 mm from the root surface (Jones, 1998).

From the contrasts C3, C4 and C5 (Table 3), we evaluated the behavior of citric acid (CA) and malic acid (MA) in each residue. In general, citric acid promoted increased K release from the mineral structure, when compared with malic acid, for the studied residues. Citric acid is a tricarboxylic acid having one more carboxylic group than the dicarboxylic malic acid (Martins et al., 2004). These COOH groups can dissociate, thus releasing their protons and promoting chemical changes in minerals and the liberation of nutrients.

The effect of organic acids rates (CA – citric acid; MA – malic acid) on K release from the ornamental rock residues (R1, R2 and R3) is shown in figures 2 and 3. Potassium liberation from the rock residue was highest in the first three collections, significantly responding to the organic acid rates applications. The application of increasing rates of citric acid promoted an increase in the release rate of K from the ornamental rock residues (Figure 2), resulting in higher K liberation from R1, followed by R2 and R3.

The increased K release of R1 becomes less apparent over time (Figure 2). The effect of K liberation using oxalic acid in Chinese soils and minerals and indicated that the ability of oxalic acid to release K depends mainly on the solution pH was observed by Tu et al. (2007).

Malic acid rates applied to ornamental rock residues provided an increase in the K dissolution rate, but these were lower when compared to citric acid (Figure 3). The mineral dissolution rates exhibit a well-defined pattern, as the initial reaction rates follow a parabolic pattern and subsequently display linear behavior (Barman et al., 1992). The parabolic rates are the result of a limiting step in the diffusion rate controlled by the reaction involving the transfer of cation-ligand complexes from the solid surface into the solution, and linear dissolution in the later reaction stages is linked to the creation rate of new sites, equaling the removal rate of surface cations.

With the exception of the third collection, it was not possible to achieve regression models significant for R3 with the use of malic acid. The use of increasing rates of this residue did not favor K liberation, which is probably associated with its more weathering-resistant mineralogical composition.
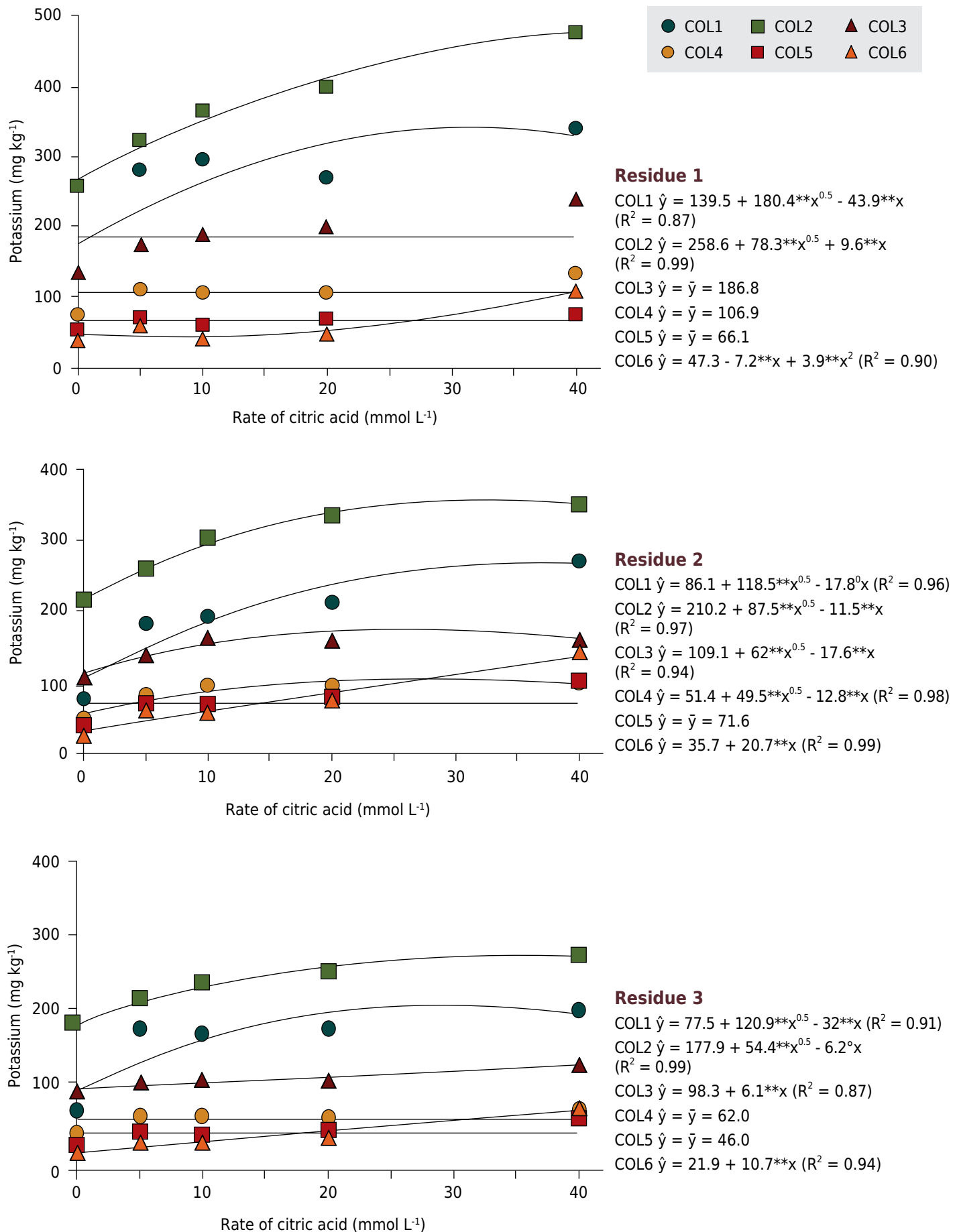
Residue 1

COL1 $\hat{y} = 139.5 + 180.4^{**}x^{0.5} - 43.9^{**}x$ $(R^2 = 0.87)$

COL2 $\hat{y} = 258.6 + 78.3^{**}x^{0.5} + 9.6^{**}x$ $(R^2 = 0.99)$

COL3 $\hat{y} = \bar{y} = 186.8$

COL4 $\hat{y} = \bar{y} = 106.9$

COL5 $\hat{y} = \bar{y} = 66.1$

COL6 $\hat{y} = 47.3 - 7.2^{**}x + 3.9^{**}x^2$ $(R^2 = 0.90)$

Residue 2

COL1 $\hat{y} = 86.1 + 118.5^{**}x^{0.5} - 17.8^{0}x$ $(R^2 = 0.96)$

COL2 $\hat{y} = 210.2 + 87.5^{**}x^{0.5} - 11.5^{**}x$ $(R^2 = 0.97)$

COL3 $\hat{y} = 109.1 + 62^{**}x^{0.5} - 17.6^{**}x$ $(R^2 = 0.94)$

COL4 $\hat{y} = 51.4 + 49.5^{**}x^{0.5} - 12.8^{**}x$ $(R^2 = 0.98)$

COL5 $\hat{y} = \bar{y} = 71.6$

COL6 $\hat{y} = 35.7 + 20.7^{**}x$ $(R^2 = 0.99)$

Residue 3

COL1 $\hat{y} = 77.5 + 120.9^{**}x^{0.5} - 32^{**}x$ $(R^2 = 0.91)$

COL2 $\hat{y} = 177.9 + 54.4^{**}x^{0.5} - 6.2^{°}x$ $(R^2 = 0.99)$

COL3 $\hat{y} = 98.3 + 6.1^{**}x$ $(R^2 = 0.87)$

COL4 $\hat{y} = \bar{y} = 62.0$

COL5 $\hat{y} = \bar{y} = 46.0$

COL6 $\hat{y} = 21.9 + 10.7^{**}x$ $(R^2 = 0.94)$

Legend: ● COL1 ■ COL2 ▲ COL3 ● COL4 ■ COL5 ▲ COL6

Axis labels: Potassium (mg kg⁻¹); Rate of citric acid (mmol L⁻¹)

Figure 2. Potassium extracted from the residues (R1, R2, R3) at six sampling times (1, 5, 10, 15, 30 and 60 days, respectively, COL1, COL2, COL3, COL4, COL5, COL6), with the application of different rates of citric acid (CA). **, * and °: significant at 1, 5 and 10 %, respectively.
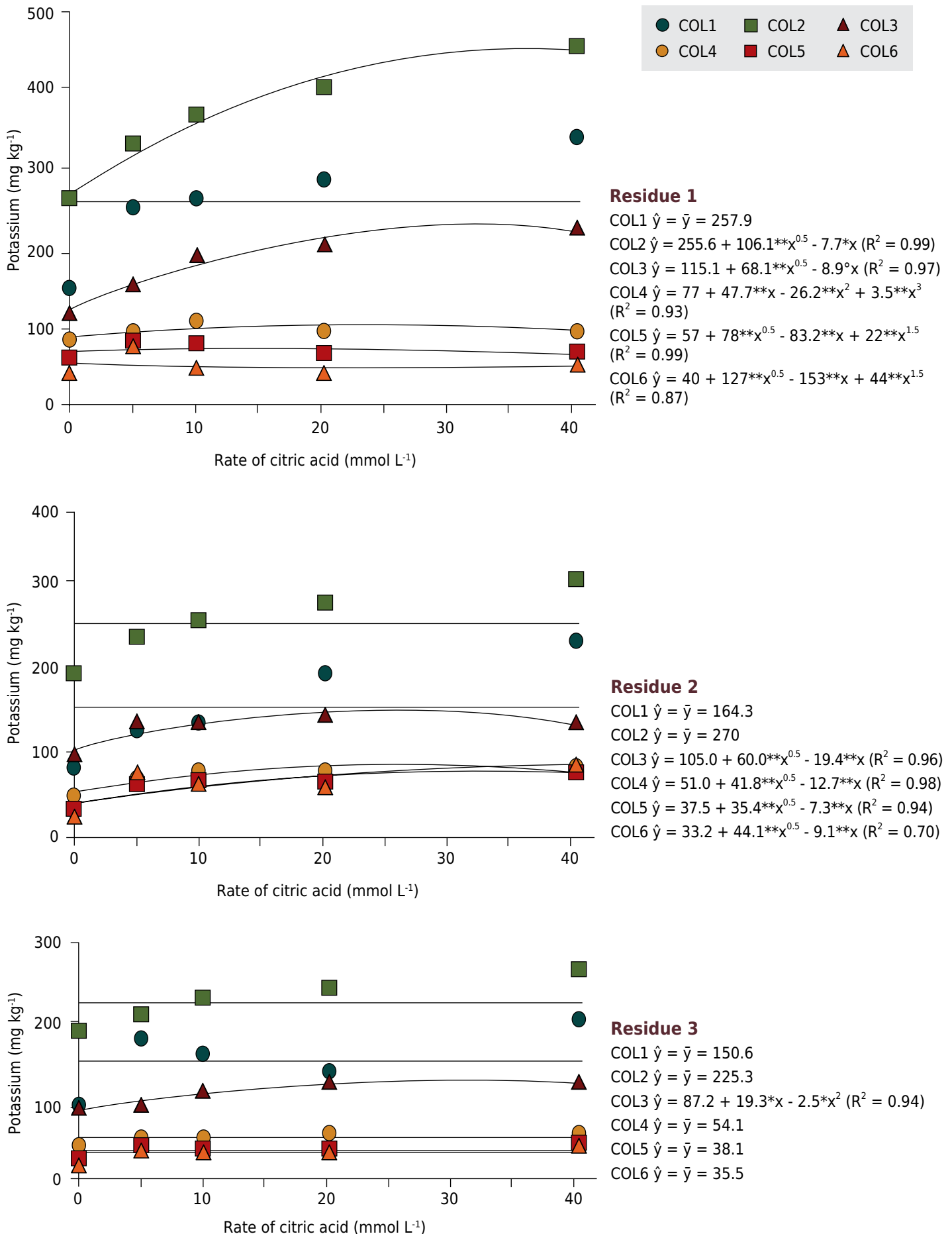
Residue 1

COL1 $\hat{y} = \bar{y} = 257.9$
COL2 $\hat{y} = 255.6 + 106.1^{**}x^{0.5} - 7.7^{*}x$ ($R^2 = 0.99$)
COL3 $\hat{y} = 115.1 + 68.1^{**}x^{0.5} - 8.9°x$ ($R^2 = 0.97$)
COL4 $\hat{y} = 77 + 47.7^{**}x - 26.2^{**}x^2 + 3.5^{**}x^3$
($R^2 = 0.93$)
COL5 $\hat{y} = 57 + 78^{**}x^{0.5} - 83.2^{**}x + 22^{**}x^{1.5}$
($R^2 = 0.99$)
COL6 $\hat{y} = 40 + 127^{**}x^{0.5} - 153^{**}x + 44^{**}x^{1.5}$
($R^2 = 0.87$)

Residue 2

COL1 $\hat{y} = \bar{y} = 164.3$
COL2 $\hat{y} = \bar{y} = 270$
COL3 $\hat{y} = 105.0 + 60.0^{**}x^{0.5} - 19.4^{**}x$ ($R^2 = 0.96$)
COL4 $\hat{y} = 51.0 + 41.8^{**}x^{0.5} - 12.7^{**}x$ ($R^2 = 0.98$)
COL5 $\hat{y} = 37.5 + 35.4^{**}x^{0.5} - 7.3^{**}x$ ($R^2 = 0.94$)
COL6 $\hat{y} = 33.2 + 44.1^{**}x^{0.5} - 9.1^{**}x$ ($R^2 = 0.70$)

Residue 3

COL1 $\hat{y} = \bar{y} = 150.6$
COL2 $\hat{y} = \bar{y} = 225.3$
COL3 $\hat{y} = 87.2 + 19.3^{*}x - 2.5^{*}x^2$ ($R^2 = 0.94$)
COL4 $\hat{y} = \bar{y} = 54.1$
COL5 $\hat{y} = \bar{y} = 38.1$
COL6 $\hat{y} = \bar{y} = 35.5$

Figure 3. Potassium extracted from the residues (R1, R2, R3) at six sampling times (1, 5, 10, 15, 30 and 60 days, respectively, COL1, COL2, COL3, COL4, COL5, COL6), with the application of different rates of malic acid (MA). **, * and °: significant at 1, 5 and 10 %, respectively.

Citric and malic acids extracted higher K concentrations at 5 days (COL 2), demonstrating that extraction took place in the early days of collection. The amount of organic acid that promoted the highest K extraction from the residues occurred in a range from 20 to 40 mmol L^{-1}, for both organic acids.

CONCLUSIONS

The citric and malic acids increased the liberation of K from ornamental rock residue, and the citric acid resulted in more K liberation when compared with malic acid.

The organic acid solutions were efficient in liberating K from ornamental rock residue in the initial days of the experiment, and the ornamental rock residue liberated, via the action of citric and malic acids, the most part of the K quantified at the end of the experiment.

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